Remediating dicamba-contaminated water with zerovalent iron

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Abstract

Dicamba (3,6-dichloro-2-methoxybenzoicacid) is a highly mobile pre- and post-emergence herbicide that has been detected in ground water. We determined the potential of zerovalent iron (Fe^0) to remediate water contaminated with dicamba and its common biological degradation product, 3,6-dichlorosalicylic acid (DCSA). Mixing an aqueous solution of 100 μM dicamba with 1.5% Fe^0 (w/v) resulted in 80% loss of dicamba within 12 h. Solvent extraction of the Fe^0 revealed that dicamba removal was primarily through adsorption; however when the Fe^0 was augmented with Al or Fe(III) salts, dicamba was dechlorinated to an unidentified degradation product. In contrast to dicamba, Fe^0 treatment of DCSA resulted in removal with some dechlorination observed. When DCSA was treated with Fe^0 plus Al or Fe(III) salts, destruction was 100%. Extracts of this Fe^0 treatment contained the same HPLC degradation peak observed with the Fe^0 + Al or Fe(III) salt treatment of dicamba. Molecular modeling suggests that differences in removal and dechlorination rates between dicamba and DCSA may be related to the type of coordination complex formed on the iron surface. Experiments with ^{14}C-labeled dicamba confirmed that Fe-adsorbed dicamba residues are available for subsequent biological mineralization (11% after 125 d). These results indicate that Fe^0 could be potentially used to treat dicamba and DCSA-contaminated water.
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1. Introduction

Dicamba (3,6-dichloro-2-methoxybenzoicacid) is a low-cost herbicide used for pre- and post-emergence control of annual and perennial broadleaf weeds. With a pK_a of 1.87, dicamba is anionic and weakly adsorbed at ambient soil pH (Weed Science Society of America, 2002). Dicamba is very soluble in water (4500 mg l^{-1}; Weed Science Society of America, 2002) and considered highly mobile (Comfort et al., 1992). The primary degradation product of dicamba is 3,6-dichlorosalicylic acid

(DCSA), which occurs biologically via the demethylase enzyme under both aerobic (Yang et al., 1994) and anaerobic conditions (Milligan and Häggblom, 1996). Despite structural similarities, DCSA is much less mobile than dicamba because it is strongly sorbed by soils (Murray and Hall, 1989; Comfort et al., 1992).

Dicamba has a reported half-life of approximately 14 d in agronomic soils (Weed Science Society of America, 2002) but its dissipation may vary from 2 to 12 weeks when applied at recommended rates (Donaldson and Foy, 1965; Friesen, 1965). Degradation and transport of dicamba are largely a function of herbicide concentration (Altom and Stritzke, 1973), soil type and climatic conditions (Scifres and Allen, 1973), and time between application and the first irrigation or precipitation (Comfort et al., 1992).

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Reports of dicamba mobility have varied. Scifres and Allen (1973) detected dicamba at a depth of 120 cm in a sandy soil 53 weeks after application at 1.86 kg a.i. ha^{-1} and 380 mm of accumulated precipitation. Ritter et al. (1987) observed dicamba at a 310 cm depth within 12 d after application at 0.28 kg a.i. ha^{-1} to a loamy soil and 54 mm of rainfall. These reports indicate that if sufficient degradation does not occur, dicamba can move below the rooting zone. This high leaching potential has been confirmed by detection of dicamba in various ground waters throughout the US (Ritter, 1990).

For most organic contaminants, processes governing environmental fate include adsorption–desorption within the soil matrix, chemical and biological degradation, volatilization, and transport. Contaminant properties and site-specific characteristics largely dictate the magnitude of these processes. Compounds with large organic carbon partition coefficients (K_{oc}) will be strongly sorbed to soil organic fractions. Pesticides with a low K_{oc} such as dicamba (~ 2 l kg^{-1}; Weed Science Society of America, 2002) can move rapidly with water through the vadose zone and contaminate ground water.

The infiltration of halogenated compounds to ground water has generated considerable interest in engineering a reducing environment in soils, sediments and aquifers for remediation purposes. Under reducing conditions, many of these contaminants can be detoxified through reductive dehalogenation reactions. Copious evidence indicates that reducing or removing electron-withdrawing moieties from parent structures generally results in more biodegradable products (Hundal et al., 1997; Singh et al., 1998; Fathepure and Tiedje, 1999). Based on this premise, one technology gaining widespread acceptance is the use of zerovalent metals for remediating ground water contaminated with halogenated compounds.

The use of zerovalent metals has become an alternative to pump and treat and air-sparging technologies. The emergence of permeable reactive barriers (PRBs) containing zerovalent iron (Fe^0) cuttings has proven to be a cost-effective treatment for contaminated ground water. To date, more than 50 granular iron PRBs have been installed within the United States for the degradation of volatile organic compounds (VOCs) (Enviro-Metal Technologies Inc., 2001). Although treating chlorinated solvents with PRBs is becoming commonplace, similar treatment of pesticide-contaminated water has not been widely pursued, largely due to insufficient data on the interaction of pesticides with Fe^0.

Previous research supports the use of Fe^0 for treating water contaminated with metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide) and atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) (Singh et al., 1998; Comfort et al., 2001; Gaber et al., 2002) but earlier work by Davenport (1996) reported that dicamba

and 2,4-D (2,4-dichlorophenoxyacetic acid), two acidic pesticides, were essentially unreactive when exposed to granular iron in sacrificial batch reactors. This lack of reactivity, however, may have resulted from an alkaline pH and repulsion of the carboxylate herbicide anions from the corroding Fe^0 surface.

This study investigated the interaction of Fe^0 with dicamba and DCSA. Our objective was to determine if Fe^0 could dechlorinate dicamba and DCSA and promote biodegradation of the dechlorinated products.

2. Materials and methods

2.1. Chemical reagents

Technical-grade dicamba acid (98% purity) and 3,6-dichlorosalicylic acid (98% purity) were purchased from Chem Service, Inc. (West Chester, PA). Ring-labeled ^{14}C-dicamba (specific activity 42.2 mCi mmol^{-1}) was provided by BASF (Research Triangle Park, NC). Other chemicals were either reagent-grade (FeCl$_3 \cdot$6H$_2$O, AlCl$_3 \cdot$6H$_2$O, Fe$_2$(SO$_4$)$_3 \cdot$3H$_2$O, H$_3$PO$_4$, CaCl$_2$), HPLC-grade (acetonitrile) (Fisher Scientific, Pittsburgh, PA) or commercial-grade (Al$_2$(SO$_4$)$_3$) and used as received. The Fe^0 was unannealed iron ($\leqslant 50$ mesh cast iron aggregates; Peerless Metal Powders, Detroit, MI) with a specific surface area of 2.55 m^2 g^{-1} (Micromeritics, Norcross, GA). The iron contained approximately 2% carbon and the surface was coated with magnetite (Fe$_2^{III}$Fe^{II}O$_4$) and ferric oxides (primarily hematite, α-Fe$_2$O$_3$), as determined by Raman microspectroscopy.

2.2. Treatment of dicamba-contaminated water

Batch experiments were conducted using aqueous solutions of dicamba (1000 μM, initial pH 3.19) and various concentrations of Fe^0. Treatments were prepared in triplicate by adding 1, 3, 4, 6, 8 and 10 g of unannealed Fe^0 to 100 ml of dicamba solution (1–10% w/v) in 250 ml Erlenmeyer flasks. This yielded Fe^0 concentrations between 1% and 10% on a weight/volume (w/v) basis. Flasks were sealed with parafilm and agitated on an orbital shaker at 23 ± 2 °C. Solution pH was measured and monitored as required using a standard Ag/AgCl electrode.

Dicamba destruction kinetics were determined by removing 1 ml aliquots from the batch reactors at 0, 6, 12, 24, 36 and 48 h following Fe^0 addition and centrifuging at 15 000 × g for 10 min. An 0.80 ml aliquot of the supernatant was then removed for analysis by reverse phase high performance liquid chromatography (HPLC). HPLC operating conditions included a Keystone NA column (Keystone Scientific, Bellefonte, PA) and a mobile phase of (v/v) 30% aqueous acetonitrile/70% H$_2$O/0.125% H$_3$PO$_4$ at 1.0 ml min^{-1} (Comfort et al.,

1992), with quantification at 220 nm using a photodiode array detector. Under these conditions, typical retention times were 15 min for dicamba and 10.2 min for DCSA. The quantitative detection limit for both compounds was 0.1 mg l^{-1}.

A second batch experiment was conducted as described above using a lower initial dicamba concentration (100 μM, pH = 4.09) and a narrower Fe^0 concentration range (1.0%, 1.5%, 2.0%, 2.5%, 3.0% and 3.5% w/v). After agitating the mixture for 0, 6, 12, 24, 48 and 72 h, 1.0 ml aliquots were removed, centrifuged, and dicamba concentrations determined by HPLC. Following HPLC analysis, 0.50 ml was removed from each reactor for chloride analysis by ion chromatography (IC, Dionex DX-120, Sunnyvale, CA) using a AS14 IonPac column and 3.5 mM sodium carbonate/1.0 mM sodium bicarbonate eluent at 1.2 ml min^{-1}.

Following treatment, the dicamba solution was decanted from the iron by placing a magnet under the batch reactor. The iron was then extracted with 100 ml of 70/30 (v/v) CH$_3$CN/3 mM CaCl$_2$ by shaking for 24 h and the extract analyzed by HPLC.

2.3. Treatment of dicamba and DCSA with Fe^0 + Al and Fe salts

Aqueous solutions (100 ml) of dicamba (100 μM) and DCSA (122 μM) were treated with 1.25 g Fe^0 with and without FeCl$_3$, Fe$_2$(SO$_4$)$_3$, AlCl$_3$, and Al$_2$(SO$_4$)$_3$ (4 mM Al or Fe) in 250 ml Erlenmeyer flasks. The flasks were covered with parafilm and agitated on an orbital shaker at 23 ± 2 °C. Subsamples (1 ml) were removed at preselected times, centrifuged at 13 000 × g for 10 min and analyzed by HPLC and IC. Following treatment, the solution was decanted and the iron was immediately extracted and the extracts analyzed as previously described.

To aid in assessing the fate and distribution of the dechlorinated dicamba in the Fe^0–H$_2$O system, an additional experiment was conducted in which the dicamba solution (100 μM) was spiked with 4.11 μCi of ^{14}C-dicamba and treated with 1.5% (w/v) Fe^0 + Al$_2$(SO$_4$)$_3$ (4 mM Al). Solution ^{14}C-activity was determined by mixing 1 ml subsamples with 6 ml Ultima Gold counting solution (Packard, Meriden, CT) and liquid scintillation counting (LSC) using a Packard 1900 TR liquid scintillation counter (Packard Instrument Co., Downers Grove, IL). Dicamba was determined by HPLC and chloride by IC.

2.4. Aquifer microcosms

Recognizing that Fe^0 removed dicamba from aqueous solution by adsorption (Fe^0 alone) or adsorption and dechlorination (Fe^0 + Al^{3+} or Fe^{3+} salts), we determined the potential for further biotic transformation by placing the Fe^0 from the ^{14}C-dicamba treatment into an aquifer microcosm and measuring cumulative mineralization (^{14}CO$_2$ release). Using procedures previously described, 100 ml of ^{14}C-labeled dicamba solution (100 μM) was treated with 1.5 g Fe^0 alone, Fe^0 + FeCl$_3$, or Fe^0 + AlCl$_3$. Treatments (replicated six times) were agitated on an orbital shaker at 23 ± 2 °C for 48 h and 2 ml samples were taken to quantify dicamba and ^{14}C-remaining in solution.

Following analysis, three of the six replicates from each treatment were decanted and the iron extracted by shaking with 100 ml of 70/30 acetonitrile/3 mM CaCl$_2$ for 24 h. Two sequential, 24-h washings of the iron with 100 ml of deionized, distilled H$_2$O were also performed and all extracts were analyzed for dicamba and ^{14}C-activity. The experimental units were then decanted and the iron was air-dried. The ^{14}C-remaining on the iron was determined by combusting 0.1 g samples in a biological oxidizer (Tri-Carb B306, Packard Instrument Co.). Liberated ^{14}CO$_2$ was trapped in 3:2 (v/v) Carbosorb/Permaflour (Packard) and quantified by liquid scintillation counting (LSC).

The remaining granular Fe^0 (∼1.4 g) was added to individual wide-mouth mason jars with 10 g Ogallala formation gravels, plus 8 ml of water from the Ogallala formation. The gravels were a mixture of sediments from a fresh drilling site (118–132 and 147–154 m depths) in central Nebraska south of the Platte River, within the Ogallala Formation of the High Plains aquifer. Aquifer water, also from the Ogallala Formation, was taken from a well north of the drill site. This aquifer represents the principal source of ground water within a large agricultural area where dicamba is routinely used. A vial containing 10 ml of 0.5 M NaOH was suspended over the mixture to trap ^{14}CO$_2$ from dicamba mineralization and the lids were closed. The ^{14}CO$_2$-traps were removed and replaced after 5, 10, 15, 25, 30, 40, 55, 70, 95 and 125 d; ^{14}C-activity was determined by LSC. Cumulative mineralization was determined by summing total ^{14}C-recovered in ^{14}CO$_2$-traps during temporal samplings.

3. Results and discussion

3.1. Fe^0 treatment of dicamba-contaminated water

When pesticide spills occur, contamination can be excessive and concentrations in runoff or surface water may approach solubility limits. By contrast, when recommend herbicide rates are applied, pesticide concentrations in soil solutions are considerably less. To represent these contrasting scenarios, two initial dicamba concentrations (100 and 1000 μM) were used for experimentation. Surprisingly, our results with 1000 μM dicamba solution revealed that increasing the Fe^0

concentration actually decreased the amount of dicamba removed. Maximum dicamba loss ($\sim$90% within 48 h) occurred in the presence of 1% Fe^0 (w/v), while only 10% dicamba loss occurred during the first 48 h when 10% Fe^0 was used (Fig. 1). Few reports of Fe^0 treatment of dicamba are available in the literature, but of the two references discovered, Davenport (1996) observed no removal of dicamba when 40 g Fe^0 (VWR coarse iron fillings, 40 mesh) was used to treat 100 ml of an unbuffered dicamba solution (45 μM). The Fe^0 concentration in Davenport's experiment was fourfold higher than our highest concentration (40% vs. 10%) and his results would be consistent with the trend we observed (i.e., higher Fe^0 concentrations resulted in less dicamba removal, Fig. 1). By contrast, Ghauch (2001) used a much lower Fe^0 concentration (0.5%) and showed rapid dicamba removal (5.65 μM) when the solution was buffered at pH 6.6.

Differences in dicamba removal among the Fe^0 concentrations are likely due to differences in solution pH. Our dicamba solutions were unbuffered and all Fe^0 treatments increased the pH from 3.1 to between 5.8 and 7.3 within 48 h (Fig. 1a). The increase in pH can be
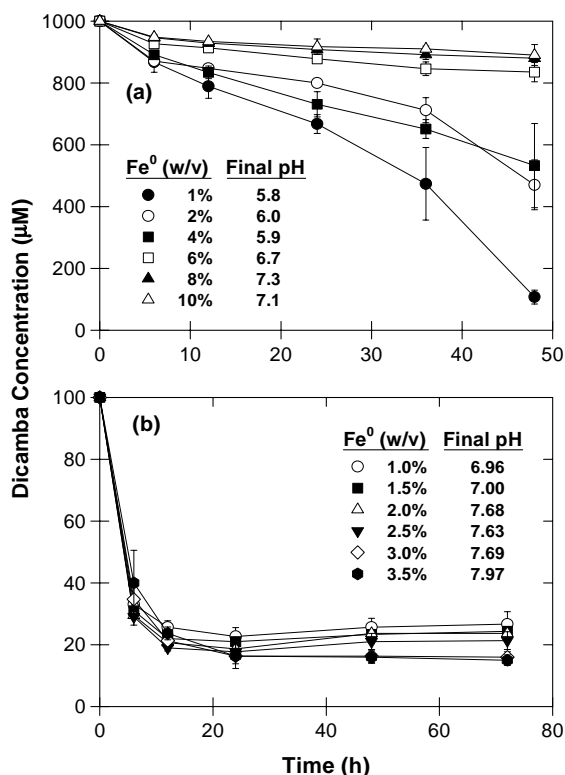
attributed to oxidative dissolution of iron metal resulting from reaction of Fe^0 with dissolved O_2 or H_2O (Scully, 1990). The 1% Fe^0 treatment had the smallest impact on pH and was most effective in removing dicamba from solution. Because the iron is corroding during treatment, the surface mineralogy is in flux and can consist of various Fe(II) and Fe(III) (hydr)oxides. Depending on the dominant (hydr)oxide formed, increasing the pH above seven may have crossed the zero point of charge (ZPC), resulting in a negatively charged surface that would repel dicamba anions. Although the higher Fe^0 concentrations provided more surface area for dicamba sorption, the more alkaline pH likely resulted in a net negative charge on the iron surface and repulsion of dicamba. Additional evidence for the influence of pH was provided in a related experiment where a pH-stat was used to maintain the pH at 4.0. In this experiment, 64% of the dicamba was removed from solution treated with 5% annealed Fe^0 (data not shown).

When we treated a lower initial dicamba concentration (100 μM) under a narrower range of Fe^0 concentrations (Fig. 1b), we observed similar dicamba removal in all iron treatments with the most rapid loss occurring during the first 12–24 h and no additional loss for the remainder of the experiment (72 h). This likely indicates equilibration and adsorption of dicamba.

For both dicamba concentrations, no new chromatographic peaks (degradation products) were observed during HPLC analysis and no chloride release was detected during Fe^0 treatment. These results indicate that dicamba was being adsorbed and not dechlorinated by the iron surface. This was verified in a companion experiment by treating a dicamba solution (100 μM) with 1.5% (w/v) Fe^0 and extracting the iron. Results indicated 80 $\pm$ 3% dicamba removal from solution (similar to Fig. 2) and 75 $\pm$ 3% of the adsorbed
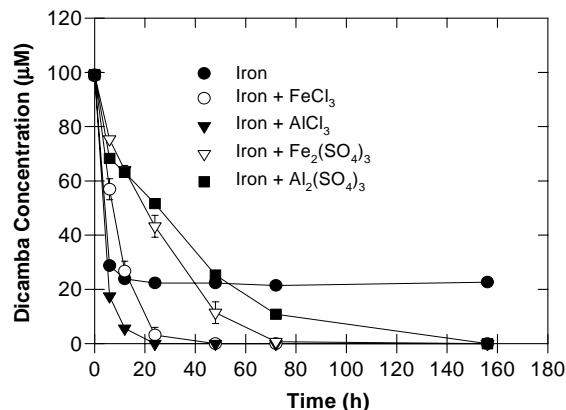

Fig. 1. Sorption of dicamba (a: 1000 μM, initial pH = 3.19; b: 100 μM, initial pH = 4.09) on varying amounts of zerovalent iron (Fe^0). Bars on symbols indicate standard deviations of means; where absent, bars fall within the symbols.

Fig. 2. Removal of dicamba (100 μM) from solution with 1.25% (w/v) Fe^0 augmented with $AlCl_3$, $FeCl_3$, $Fe_2(SO_4)_3$, or $Al_2(SO_4)_3$ (4 mM Al or Fe). Bars on symbols indicate standard deviations of means; where absent, bars fall within symbols.

dicamba was recovered in the iron extracts after treatment.

3.2. Dicamba dechlorination with Fe⁰ + Al and Fe salts

Adding Al or Fe(III) salts with Fe^0 altered the kinetics and extent of dicamba loss. When Fe^0 was used alone, dicamba was rapidly lost (75%) from solution but solution concentrations reached a plateau after 12 h indicating adsorption as the primary mechanism (Fig. 2). When $AlCl_3$ or $FeCl_3$ was added with the Fe^0, dicamba loss exceeded 95% within 24 h (Fig. 2). Dicamba loss was slower when sulfate salts were used but was complete within 156 h (Fig. 2). One possible explanation for this difference may be due to greater competition between the divalent sulfate anions and dicamba anions compared to monvalent chloride for sites on the oxidizing iron.

Chloride analysis was performed after treating ^{14}C-spiked dicamba solutions with $Fe^0 + Al_2(SO_4)_3$ (Fig. 3). After 156 h, 84% of the initial 100 μM dicamba was removed from solution and 161 μmol of Cl^- was released. Because each mole of dicamba contains two moles of Cl^-, this equates to 96% dechlorination by the $Fe^0 + Al_2(SO_4)_3$ treatment. HPLC analysis of the iron extract revealed a product peak (retention time = 4.6 min) and no dicamba was found. Because analysis of the iron extracts from the $AlCl_3$ and $FeCl_3$ treatments were similar to the $Al_2(SO_4)_3$ treatment (i.e., the same product peak and no dicamba), we believe the iron and aluminum chloride salts also facilitated dechlorination. Similar research has demonstrated that adding Al or Fe salts during Fe^0 corrosion increases metolachlor dechlorination rates (Comfort et al., 2001; Satapanajaru et al., 2003), but unlike dechlorinated dicamba, the dechlorinated metolachlor was not adsorbed. Removal of the dechlorinated dicamba product via adsorption to the iron may be desirable in permeable reactive iron barrier treatment systems.

Tracking temporal changes in ^{14}C-activity revealed that ^{14}C-concentrations mimicked dicamba concentrations (Fig. 3). This trend was observed in all treatments (not shown) and provides evidence for adsorption of both dicamba and the dechlorinated product(s). Because temporal changes in ^{14}C-activity and dicamba concentrations were nearly identical (Fig. 3), and the observed stoichiometry between dicamba and Cl^- production, it appears that dicamba is adsorbed and then dechlorinated. Evidence can be gleaned from the 36 h data where 44 μM dicamba was removed from solution and 104 μM Cl^- recovered (Fig. 3). This slightly exceeds a 1:2 ratio (dicamba/Cl^-) and supports that dicamba dechlorination occurs as it is removed from solution.

3.3. Treatment of DCSA with Fe⁰ + Al and Fe salts

Treating DCSA with Fe^0 resulted in removal kinetics resembling the 100 μM dicamba experiment, but at a faster rate (Fig. 4). Augmenting Fe^0 with $AlCl_3$ or $FeCl_3$ increased the kinetics of DCSA removal from solution (Fig. 4). With all salts tested, DCSA removal was 100% but different removal rates were observed among the salts: $FeCl_3 > Fe_2(SO_4)_3 > AlCl_3 > Al_2(SO_4)_3$. Rapid initial DCSA loss with Fe^0 alone was followed by a gradual decline but incomplete removal at 24 h, while removal was essentially complete within 12 h for treatments receiving Al and Fe salts. Similar removal kinetics have been reported for salicylate on alumina colloids (Stumm et al., 1980). In a companion experiment where DCSA was treated with 1% Fe^0 for 44 h, we recovered 20% of DCSA chloride in solution, indicating that DCSA can be dechlorinated by Fe^0 alone (data not shown). Extraction of the iron after treatment revealed the same new (degradation product) HPLC peak found in extracts of the Al augmented Fe^0 after treating dicamba. The occurrence of a post-treatment peak with the same retention time and matching UV spectrum in both the Fe^0-treated DCSA and dicamba treated with $Fe^0 + Al$ or
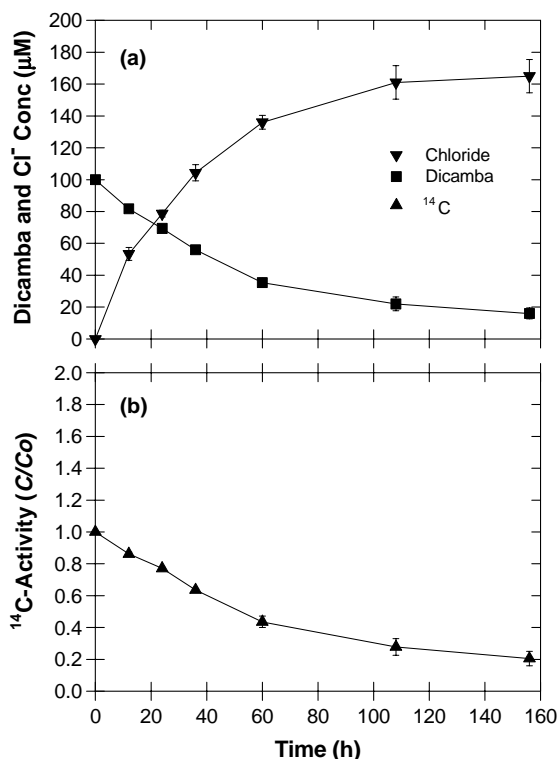

Fig. 3. Removal of (a) dicamba (100 μM) and (b) ^{14}C-activity from solution and chloride release during treatment of ^{14}C-dicamba with 1.5% (w/v) $Fe^0 + Al_2(SO_4)_3$ (4 mM Al). Bars on symbols indicate standard deviation of means; where absent, bars fall within symbols.
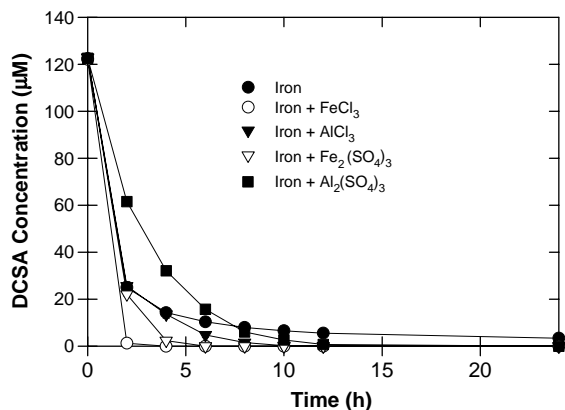
Fig. 4. Removal of DCSA (122 μM) from aqueous solution by Fe^0 with and without Al or Fe(III) salts (4 mM Al or Fe). Error bars fall within symbols.

Fe(III) salts indicates demethylation of the dicamba methoxy group, as reported for reaction of guaiacol (*o*-methoxyphenol) with Fe^{3+} (Pracht et al., 2001). Efforts to identify the unknown product have not been successful although we eliminated 2-methoxybenzoicacid, salicylic acid (the dechlorinated analogs of dicamba and DCSA) and many simple organic acids potentially resulting from cleavage of the benzene ring. Ghauch (2001) postulated that Fe^0 treatment of dicamba would produce 2-methoxybenzoicacid (dechlorinated dicamba) followed by 2-hydroxybenzoicacid (salicylic acid or dechlorinated DCSA) and finally 2-hydroxybenzylalcohol.

Past research has established that under methanogenic conditions, dicamba degradation proceeds through *O*-demethylation to DCSA and formation of 6-chlorosalicylate is then favored (Taraban et al., 1993; Milligan and Häggblom, 1999). Although possible reaction intermediates, neither 6- nor 3-chlorosalicylate were identified in our treated samples. Milligan and Häggblom (2001) observed reductive dehalogenation of 3-chlorosalicylate to salicylate in methanogenic enrichment cultures, which was then utilized, while 6-chlorosalicylate was transformed to a product that was not successfully identified.

Reasons why dicamba was not dechlorinated by Fe^0 alone but DCSA was may be related to differences between coordination of carboxylates and salicylates on metal surfaces. Past research has established that metal-bound carboxylate complexes can either be "monodentate mononuclear" (one oxygen of carboxylate binds to one metal), "bidentate mononuclear" (carboxylate forms two bonds with one metal) or "binuclear bridging" (carboxylate forms two bonds with two metals). Salicylate, however, is believed to form a monodentate, mononuclear complex with respect to the carboxylate group and a bidentate mononuclear complex with respect to the entire salicylate anion (one oxygen of car-

boxylate and phenolic group form two bonds with one metal (Yost et al., 1990). This chelated orientation would likely bring the DCSA closer to the iron surface than dicamba and possibly orient the molecule in a position favoring dechlorination. We used molecular modeling software (Spartan 02, Wavefunction, Inc., Irvine, CA) to compare dicamba and DCSA binding to an iron surface. By bonding deprotonated forms of dicamba and DCSA through a bidentate mononuclear complex and minimizing strain energies through preliminary structure refinement, our results illustrate that DCSA would be more parallel to the iron surface whereas dicamba would be more perpendicular (Fig. 5). This orientation would also appear to favor removal of the chlorine at the 3-carbon position over the 6-carbon chlorine.

Recognizing that dicamba was not dechlorinated by Fe^0 alone, how did the addition of Al^{3+} or Fe^{3+} salts change dicamba removal from adsorption to dechlorination? Earlier research has shown that adding Al^{3+} and Fe^{3+} increases dicamba adsorption on soil colloids (Murray and Hall, 1989). The presence of aluminum on the corroding iron surface would increase the Lewis acidity of the surface as well as the surface acidity, resulting in greater adsorption of dicamba anions. We also know from previous experiments that the added aluminum is quickly removed from solution in Fe^0–H$_2$O systems and that Fe^{2+} is released (Satapanajaru et al., 2003). Moreover, a high Al concentration slows down Fe(II) oxidation, favoring precipitation of Al-ferrihydrite (Taylor and Schwertmann, 1978). In the presence of Fe^{2+}, poorly crystalline mixed Al-ferric hydroxides with large surface areas may increase the number of reactive Fe(II) sites for dicamba adsorption and dechlorination. Demethylation of the dicamba methoxy
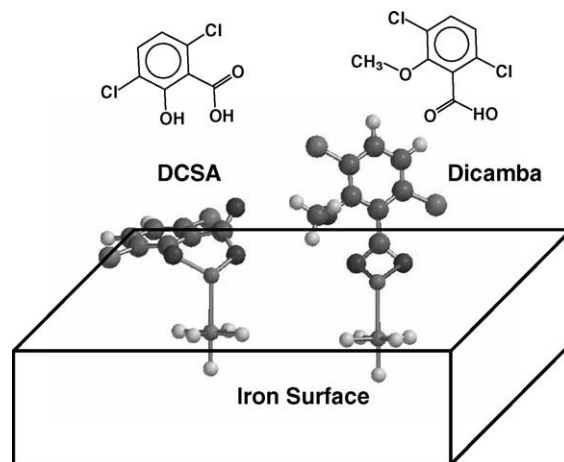

Fig. 5. Molecular model illustrating the configuration of DCSA and dicamba on an iron surface through bidentate mononuclear complexes.

group may also be occurring in treatments containing $Fe^0 + Al$ or $Fe(III)$ salts, producing DCSA, which molecular modeling suggests is adsorbed in an orientation more favorable to dechlorination.

3.4. Mineralization of ^{14}C-dicamba

Permeable reactive iron barriers have been highly effective for treating chlorinated solvents but this same technology has yet to include routine treatment of pesticide-contaminated ground water. Our batch experiments indicated that dicamba and DCSA were removed from solution by sorption and/or dechlorination; in both cases, adsorption of residues occurred. Because residues from dicamba are adsorbed by the Fe^0, the migration of toxic intermediates away from a PRB does not appear to be an issue. However, for this technique to be successful at the field scale, it is important to know whether the

adsorbed dicamba residues would be subject to further biodegradation. To test this hypothesis, Fe^0 containing adsorbed ^{14}C (dicamba and/or its transformation products) was added to microcosms of sediment and ground water from the Ogallala Formation.

Periodic monitoring for 125 d indicated cumulative $^{14}CO_2$ production (mineralization) between 4% and 11% (Fig. 6). Our earlier results confirmed that when Fe^0 alone was used, the adsorbed residue was primarily dicamba. This treatment yielded the lowest mineralization (4% for extracted iron and 7% for unextracted iron, Fig. 6). By comparison, iron from the $Fe^0 + AlCl_3$ treatment, which did not contain adsorbed dicamba but contained the dicamba dechlorination product(s), produced the greatest mineralization (8–11%). This indicates that the dechlorinated products are more prone to subsequent biodegradation. Similar observations were made in comparing degradation rates between metolachlor and dechlorinated metolachlor (Comfort et al., 2001). In another study, Singh et al. (1998) reported 11% mineralization of atrazine after 120 d in microcosms containing contaminated soil and Fe^0 compared to 4% in the absence of Fe^0. As observed with dicamba, the treatment products from atrazine were associated with the iron surface. This indicates that residues adsorbed to the corroding iron are available for subsequent biotic transformations.

Acknowledgements

Fig. 6. ^{14}C-Dicamba mineralization in Ogallala formation gravels and ground water (10 g + 8 ml) after treatment with Fe^0. Bars on symbols indicate sample standard deviations; where absent, bars fall within symbols.

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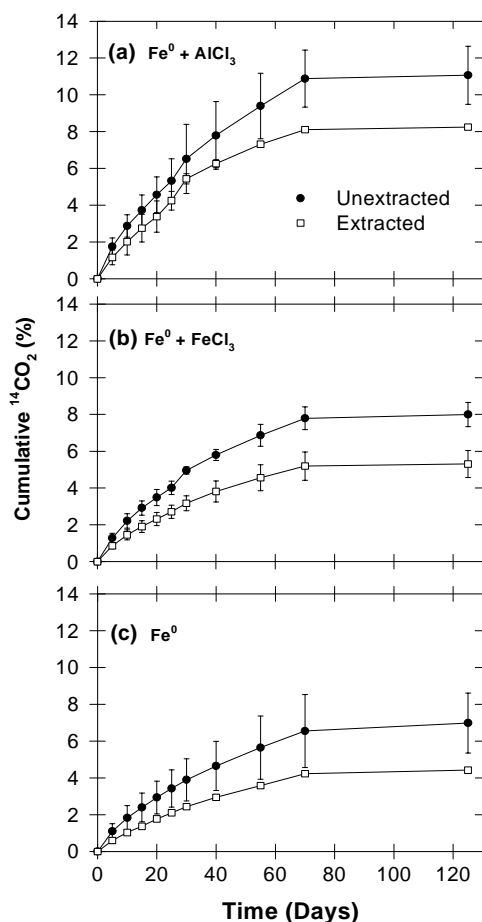
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